

Experimental study on the fractionation of yttrium from holmium during the coprecipitation with calcium carbonates in seawater solutions

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The partitioning of Y and Ho between CaCO₃ (calcite and aragonite respectively) and seawater was experimentally investigated at 25°C and 1 atm. Both Y and Ho were observed to be strongly partitioned into the overgrowths of calcite or aragonite. Their partition coefficients, D_Y and D_{Ho} , were determined to be ~520–1400 and ~700–1900 in calcite, ~1200–2400 and ~2400–4300 in aragonite, respectively. Y fractionates from Ho during the coprecipitation with either calcite or aragonite. Within our experimental conditions, the fractionation factor, $k = D_Y/D_{Ho}$, was determined to be ~0.62–0.77 in calcite and ~0.50–0.57 in aragonite, respectively. The aqueous complexation of Y and Ho, which is a function of solution chemistry, probably plays an important role in both the partitioning and the fractionation. Further analyses suggest that the difference in covalency between Y and Ho associated with changes in their coordination environments is the determinant factor to the Y–Ho fractionation in the H₂CO₃–CaCO₃ system.

Keywords: partitioning, fractionation, calcium carbonates, seawater, Y/Ho ratios, covalency

INTRODUCTION

The distribution of yttrium and rare earth elements (YREEs) in modern seawater has been widely reported (e.g., Nozaki and Alibo, 2003 and references therein). They have proven to be effective tracers of seawater chemistry (Elderfield, 1988). Among YREEs, Y and Ho show the closest similarity due to their almost identical ionic radii (0.90 Å and 0.901 Å, sixfold coordinated; Shannon, 1976), thereby often compared as geochemical twins. The Y/Ho ratio in most of geological samples is well constrained and equal to the chondritic value of 28 (Anders and Grevesse, 1989). However, the Y/Ho ratio of modern seawater is particularly high and generally falls into the range of 44–74 (super-chondritic ratio; Kawabe *et al.*, 1991; Bau, 1996; Nozaki *et al.*, 1997). It is notable that the Y/Ho ratio of fresh water in estuarine zones still remains close to the chondritic value (Nozaki *et al.*, 2000; Lawrence and Kamber, 2006; Censi *et al.*, 2007). Such a contrast, as suggested by Nozaki *et al.* (1997), probably results from the fractionation of Y from Ho during the removal by particulates. They estimated that Ho is scav-

enged two times faster than Y.

Super-chondritic Y/Ho ratios were also reported in sedimentary calcite precipitates (e.g., Webb and Kamber, 2000; Kamber and Webb, 2001; Van Kranendonk *et al.*, 2003; Kamber *et al.*, 2004; Nothdurft *et al.*, 2004), suggesting that seawater YREE signatures are retained in such precipitates. However, several processes have been not yet clarified: 1) whether Y fractionates from Ho during the incorporation, 2) what is the degree of the fractionation if any, and 3) which factors may affect the fractionation. The Y–Ho fractionation is difficult to assess from available field data. Relative experimental studies are thereby of particular importance.

Most recently, it has been experimentally proven that Y fractionates from Ho during their coprecipitation with calcite (Tanaka *et al.*, 2004, 2008; Tanaka and Kawabe, 2006). These studies show that the uptake of Ho by calcite is also faster than that of Y. The fractionation factor (D_Y/D_{Ho} , where D is the partition coefficient) was determined to fall into the range of 0.49–0.71. However, the applicability of such results to seawater is still very limited, since the experiments were not conducted under seawater conditions. Indeed, the Y–Ho fractionation appeared to be variable with experimental conditions. Furthermore, there are not available data for aragonite. Lack of data for aragonite is particularly serious in coral stud-

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Table 1. Primary parameters of our experiments (C for calcite and A for aragonite)

| ID | W_{seed} g | T hour | $W_{\text{sol'n}}$ g | At_0 mM | At_s mM | pH ^(a) | [Ca] mM | Ω ^(a) | $W_{\text{overg.}}$ g | R $\mu\text{mol hr}^{-1}\text{m}^{-2}$ |
|--------------------|------------------------|-------------|-------------------------|--------------|--------------|-------------------|------------|-------------------------|--------------------------|---|
| C1 ^(b) | 0.5998 | 29.9 | 354.5 | 3.088 | 3.006 | 7.64 | 9.844 | 2.1 | 0.0015 | 1.07 |
| C2 ^(b) | 0.6005 | 29.9 | 366.3 | 3.081 | 2.948 | 7.62 | 9.819 | 1.9 | 0.0024 | 1.78 |
| C3 | 0.6001 | 23.7 | 338.4 | 3.483 | 3.402 | 7.68 | 9.826 | 2.6 | 0.0014 | 1.26 |
| C4 | 0.5999 | 23.7 | 350.0 | 3.497 | 3.407 | 7.68 | 9.759 | 2.5 | 0.0016 | 1.45 |
| C5 | 0.5997 | 16.6 | 418.5 | 4.037 | 3.904 | 7.75 | 9.769 | 3.4 | 0.0028 | 3.69 |
| C6 | 0.6005 | 16.6 | 429.6 | 4.036 | 3.859 | 7.72 | 9.767 | 3.1 | 0.0038 | 5.01 |
| C7 | 0.6007 | 9.9 | 365.2 | 4.426 | 4.273 | 7.68 | 9.820 | 3.2 | 0.0028 | 6.22 |
| C8 | 0.5997 | 9.9 | 384.1 | 4.416 | 4.360 | 7.66 | 9.880 | 3.2 | 0.0011 | 2.38 |
| C9 | 0.6004 | 7.6 | 456.4 | 5.185 | 5.036 | 7.72 | 9.811 | 4.2 | 0.0034 | 9.79 |
| C10 | 0.6002 | 7.6 | 486.0 | 5.209 | 4.997 | 7.71 | 9.783 | 4.0 | 0.0052 | 14.9 |
| C11 | 0.6008 | 96.2 | 357.3 | 2.668 | 2.633 | 7.50 | 9.876 | 1.4 | 0.0006 | 0.12 |
| C12 | 0.6006 | 96.2 | 261.2 | 2.677 | 2.640 | 7.46 | 9.888 | 1.3 | 0.0005 | 0.11 |
| C13 | 0.6000 | 6.6 | 441.9 | 5.900 | 5.614 | 7.76 | 9.745 | 5.1 | 0.0063 | 20.9 |
| C14 | 0.6004 | 6.6 | 465.2 | 5.909 | 5.601 | 7.78 | 9.795 | 5.3 | 0.0072 | 23.6 |
| A1 ^(b) | 0.6009 | 33.0 | 414.3 | 5.441 | 4.868 | 7.84 | 9.405 | 2.6 | 0.0119 | 7.76 |
| A2 | 0.6011 | 33.0 | 404.5 | 5.415 | 4.898 | 7.81 | 9.434 | 2.5 | 0.0104 | 6.82 |
| A3 | 0.6004 | 88.2 | 369.3 | 3.383 | 3.296 | 7.65 | 9.710 | 1.3 | 0.0016 | 0.40 |
| A4 | 0.6007 | 88.2 | 359.6 | 3.349 | 3.276 | 7.68 | 9.562 | 1.4 | 0.0013 | 0.32 |
| A5 | 0.5999 | 40.3 | 386.4 | 3.906 | 3.743 | 7.73 | 9.538 | 1.8 | 0.0031 | 1.69 |
| A6 | 0.5992 | 40.3 | 376.7 | 3.893 | 3.743 | 7.73 | 9.558 | 1.8 | 0.0028 | 1.52 |
| A7 | 0.5998 | 28.8 | 429.3 | 4.750 | 4.424 | 7.78 | 9.494 | 2.4 | 0.0070 | 5.26 |
| A8 | 0.5999 | 28.8 | 411.1 | 4.775 | 4.477 | 7.77 | 9.526 | 2.4 | 0.0061 | 4.59 |
| A9 | 0.5997 | 21.8 | 481.7 | 5.381 | 4.994 | 7.80 | 9.483 | 2.8 | 0.0093 | 9.26 |
| A10 | 0.6002 | 21.8 | 469.8 | 5.377 | 4.998 | 7.82 | 9.495 | 2.9 | 0.0089 | 8.82 |
| A11 ^(b) | 0.5990 | 14.6 | 467.5 | 6.036 | 5.368 | 7.85 | 9.445 | 3.3 | 0.0156 | 23.2 |
| A12 | 0.6002 | 14.6 | 463.3 | 6.044 | 5.422 | 7.84 | 9.342 | 3.2 | 0.0144 | 21.3 |
| A13 | 0.5997 | 10.1 | 479.9 | 6.887 | 6.148 | 7.89 | 9.289 | 3.9 | 0.0177 | 38.1 |
| A14 | 0.5999 | 10.1 | 469.1 | 6.880 | 6.287 | 7.87 | 9.334 | 3.8 | 0.0139 | 29.9 |

^(a)pH was measured using a combination electrode calibrated against NBS buffer solutions. The saturation state of calcite or aragonite (Ω) was calculated by pH and carbonate alkalinity based on their corresponding solubility products.

^(b)Interrupted reactions due to the attenuation of gas pressure.

ies. These aragonite precipitates have been often indicated as potential proxies of seawater YREE chemistry (e.g., Sholkovitz and Shen, 1995; Fallon *et al.*, 2002; Akagi *et al.*, 2004; Wyndham *et al.*, 2004).

The objective of this paper is thus to quantitatively evaluate the fractionation of the Y–Ho pair during their coprecipitation with calcium carbonates (CaCO_3 , calcite and aragonite respectively) in seawater.

METHODS

The “constant-addition” experimental system developed by Zhong and Mucci (1993) was used. Teflon[®] vessels and tubes were employed as much as possible to minimize adsorption phenomena. All experiments were performed in aged artificial seawater ($S = 35$, Kester *et al.*, 1967) to avoid unnecessary corrections. During each experiment, the pH of reacting solutions was maintained constant by the continuous bubbling of CO_2/N_2 gas mixture ($p\text{CO}_2 = 0.3\%$). Seed materials of calcite used in

experiments were ultrapure commercial products of Sigma-Aldrich[®], while those of aragonite were synthesized in the laboratory following the procedure of Wray and Daniels (1957) as modified by Katz *et al.* (1972) at 70°C. Both materials were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and found to be pure calcite and pure aragonite, respectively.

Two groups of experiments (25°C and 1 atm), one for calcite and one for aragonite, were arranged at different saturation states (Table 1) to examine the potential effects of solution chemistry or precipitation rates on the fractionation of the Y–Ho pair. It should be noted that the initial concentrations of Y and Ho ($[\text{Y}]_{\text{init.}}$ and $[\text{Ho}]_{\text{init.}}$, Table 2) of calcite experiments are about one order of magnitude lower than those of aragonite in order to: 1) avoid inhibition of the precipitation of calcite or aragonite; 2) make the Y (Ho) concentration in steady solutions measurable. The crystallographic characteristics of freshly formed overgrowths are in accord with those of Mg–calcite and aragonite, respectively.

Table 2. The partitioning of Y and Ho and the fractionation of the Y–Ho pair

| ID | [Y] _{init.} ^(a) nM | [Ho] _{init.} ^(a) nM | [Y] _{sol'n} nM | [Ho] _{sol'n} nM | X _Y μM | X _{Ho} μM | D _Y | D _{Ho} | k |
|--------------------|---|--|----------------------------|-----------------------------|----------------------|-----------------------|----------------|-----------------|------|
| C1 ^(b) | 7.0 ± 0.4 | 2.4 ± 0.1 | 1.91 | 0.55 | 927 | 375 | 478 | 670 | 0.71 |
| C2 ^(b) | " | " | 1.91 | 0.52 | 521 | 206 | 268 | 388 | 0.69 |
| C3 | " | " | 1.01 | 0.27 | 1,412 | 521 | 1,373 | 1,909 | 0.72 |
| C4 | " | " | 1.16 | 0.32 | 1,178 | 442 | 993 | 1,344 | 0.74 |
| C5 | " | " | 0.94 | 0.25 | 846 | 314 | 877 | 1,235 | 0.71 |
| C6 | " | " | 0.63 | 0.16 | 649 | 241 | 1,008 | 1,442 | 0.70 |
| C7 | " | " | 1.35 | 0.37 | 721 | 265 | 524 | 703 | 0.75 |
| C8 | " | " | 1.57 | 0.45 | 1,602 | 605 | 1,009 | 1,318 | 0.77 |
| C9 | " | " | 0.79 | 0.21 | 789 | 306 | 985 | 1,416 | 0.70 |
| C10 | " | " | 0.81 | 0.22 | 550 | 207 | 665 | 903 | 0.74 |
| C11 | " | " | 2.70 | 0.67 | 1,833 | 736 | 671 | 1,091 | 0.62 |
| C12 | " | " | 1.92 | 0.46 | 2,085 | 768 | 1,076 | 1,645 | 0.65 |
| C13 | " | " | 0.61 | 0.16 | 399 | 151 | 641 | 897 | 0.71 |
| C14 | " | " | 0.59 | 0.16 | 383 | 143 | 637 | 883 | 0.72 |
| A1 ^(b) | 57.1 ± 3.8 | 26.4 ± 2.0 | 1.93 | 0.72 | 1,719 | 799 | 836 | 1,042 | 0.80 |
| A2 | " | " | 1.00 | 0.24 | 1,832 | 847 | 1,727 | 3,277 | 0.53 |
| A3 | " | " | | | Sample missing | | | | |
| A4 | " | " | 7.60 | 1.77 | 9,837 | 4,466 | 1,237 | 2,407 | 0.51 |
| A5 | " | " | 3.73 | 0.79 | 5,190 | 2,219 | 1,326 | 2,670 | 0.50 |
| A6 | " | " | 3.59 | 0.79 | 5,700 | 2,405 | 1,516 | 2,921 | 0.52 |
| A7 | " | " | 1.60 | 0.37 | 3,198 | 1,401 | 1,893 | 3,590 | 0.53 |
| A8 | " | " | 2.09 | 0.49 | 3,440 | 1,556 | 1,567 | 3,020 | 0.52 |
| A9 | " | " | 1.35 | 0.33 | 2,623 | 1,178 | 1,841 | 3,347 | 0.55 |
| A10 | " | " | 1.12 | 0.28 | 2,786 | 1,252 | 2,356 | 4,254 | 0.55 |
| A11 ^(b) | " | " | 0.93 | 0.19 | 1,522 | 676 | 1,543 | 3,295 | 0.47 |
| A12 | " | " | 1.01 | 0.25 | 1,686 | 779 | 1,559 | 2,863 | 0.54 |
| A13 | " | " | 0.65 | 0.17 | 1,595 | 728 | 2,275 | 3,988 | 0.57 |
| A14 | " | " | 0.92 | 0.24 | 1,932 | 905 | 1,951 | 3,482 | 0.56 |

^(a)N = 4. The samples were analyzed together with those of steady solutions but without preconcentration.

^(b)Interrupted reactions. The relative results were listed but excluded from statistics.

When each group of experiments were finished, the total alkalinity of input solutions (At_0 , in mM) and steady solutions (At_s , in mM) was determined following the method of Zhong and Mucci (1993). Thereafter, the mass of overgrowths ($W_{\text{overg.}}$, in gram) and the precipitation rate (R , $\mu\text{mole m}^{-2}\text{hr}^{-1}$) were calculated as:

$$W_{\text{overg.}} = W_{\text{sol'n}} \times (At_0 - At_s) / 2000 \quad (1)$$

and

$$R = \frac{W_{\text{sol'n}} \times (At_0 - At_s)}{2STW_{\text{seed}}}, \quad (2)$$

where $W_{\text{sol'n}}$ is the total mass of steady solutions in gram; S is the specific surface area of seed materials in m^2/g

($0.771 \text{ m}^2/\text{g}$ for aragonite and $0.760 \text{ m}^2/\text{g}$ for calcite); T is the duration in hour and W_{seed} is the weight of seed materials. The precision of alkalinity titrations was better than $\pm 0.25\%$ when $At = 2 \text{ mM}$, which ensured that the relative errors of $W_{\text{overg.}}$ were generally restricted within 20% ($At_s/At_0 = 90\sim 96\%$, $At_0 = 3.9\sim 6.9 \text{ mM}$). For those experiments conducted near equilibrium, the difference between At_s and At_0 is very limited ($\sim 2\%$ of At_0 , relatively) and lead to exceptionally large errors in $W_{\text{overg.}}$ (50% or even larger, relatively).

Both the acidified steady reacting solutions ($\text{pH} \approx 1.6$) and collected solid samples (overgrowths + seed materials) were analyzed by off-line chelation and ICP-MS (Liu *et al.*, 2007). The off-line chelation system was built based on an ion chromatogram (Dionex[®], ICS 2500) to eliminate alkali metals and alkaline-earth metals from seawater while retain YREEs on chelation columns (Dionex[®], CC-

1). Steady solutions were treated by the off-line chelation system with a preconcentration factor of 10, which ensured that the relative errors of $[Y]_{\text{sol'n}}$ and $[\text{Ho}]_{\text{sol'n}}$ were restricted within 10%. Meanwhile, about 0.2 g solid samples were dissolved in ~ 20.0 g 1.5 wt% HNO_3 . Obtained solutions were also treated by offline chelation to eliminate Ca^{2+} but without preconcentration. Y and Ho concentrations in the solid samples ($[Y]_{\text{solid}}$ and $[\text{Ho}]_{\text{solid}}$) were revised to their molar fractions in the overgrowths (X_Y and X_{Ho}) as:

$$X_Y(X_{\text{Ho}}) = [Y]_{\text{solid}}([\text{Ho}]_{\text{solid}}) \frac{W_{\text{seed}} + W_{\text{overg.}}}{W_{\text{overg.}}} \quad (3)$$

The concentrations of Y and Ho in raw seed materials, as determined by the same method, are at least 3 orders of magnitude lower than $[Y]_{\text{solid}}$ and $[\text{Ho}]_{\text{solid}}$ and thus have no influence on the calculation of X_Y and X_{Ho} . Finally, partition coefficients of Y (D_Y) and Ho (D_{Ho}) between CaCO_3 overgrowths and seawater solutions were calculated as:

$$D_{Y(\text{Ho})} = \frac{\left(\frac{X_{Y(\text{Ho})}}{X_{\text{Ca}}} \right)_{\text{overg.}}}{\left(\frac{[Y(\text{Ho})]}{[\text{Ca}]} \right)_{\text{sol'n}}}, \quad (4)$$

where $[\text{Ca}]$ denotes the concentration of Ca^{2+} in steady solutions determined by titrations ($1\sigma = \pm 0.5\%$, when $[\text{Ca}] = 10$ mM). Among all the effective factors, the precision of D_Y or D_{Ho} is dominated by that of $W_{\text{overg.}}$. On the other hand, the fractionation of the Y–Ho pair was quantified by the fractionation factor as:

$$k = \frac{D_Y}{D_{\text{Ho}}}. \quad (5)$$

Since k is the ratio between D_Y and D_{Ho} , the large errors of D_Y and D_{Ho} inherited from $W_{\text{overg.}}$ were eliminated. The uncertainties of k thereby are dependent on those of $[Y]_{\text{sol'n}}$ and $[\text{Ho}]_{\text{sol'n}}$.

RESULTS AND DISCUSSION

The precipitation of CaCO_3

As allomorphs of CaCO_3 , the precipitation of calcite and aragonite in seawater is affected by various factors, such as solution chemistry and temperature (Morse, 1983). For any experiments involving both calcite and aragonite, the crystal characterization is absolutely necessary.

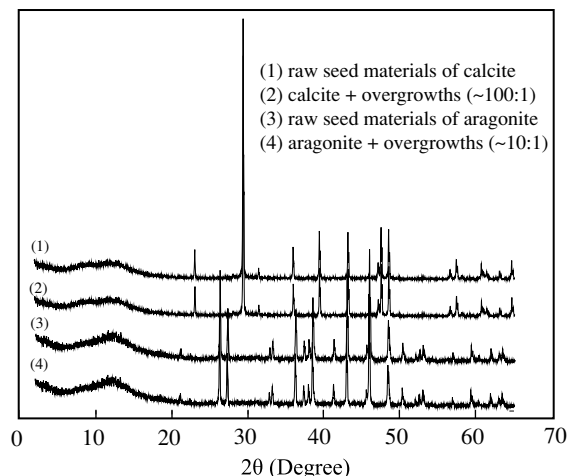


Fig. 1. XRD spectrum of raw seed materials and collected solid samples (seed materials + overgrowths).

Therefore, collected solid samples (seed materials + overgrowths) were re-examined by XRD and SEM in this study, while no difference were observed between such solids and raw seed materials. Since it is likely resulting from the limited amount of overgrowths formed in our experiments, we performed further ICP-MS tests on our samples after direct dilution. The overgrowths of calcite experiments were observed to contain a considerable molar fraction of Mg ($\sim 8\%$), which enable us to confirm such overgrowths as Mg–calcite. However, as that adopted by Zhong and Mucci (1995), we conventionally classified Mg–calcite as calcite in this paper hereafter. To identify the crystallographic characteristics of overgrowths formed in our aragonite experiments, a long term experiment of aragonite, beginning with a saturation state of ~ 9 (Ω_a), was particularly conducted by the free-drift method (Nancollas *et al.*, 1981). The mass of overgrowths was estimated to be ~ 0.05 g and there is no difference between collected solid samples and raw aragonite seed materials (Fig. 1). Hence, it can be concluded that aragonite precipitated in these experiments.

For experimental studies on (Y)REE coprecipitation with CaCO_3 , the level of (Y)REE concentration needs to be monitored. It has proven that the presence of (Y)REEs at high dissolved concentrations can severely inhibit the precipitation of calcite (e.g., Zhong and Mucci, 1995; Tanaka *et al.*, 2004; Tanaka and Kawabe, 2006). In this study, we once attempted to set $[Y]_{\text{init.}}$ and $[\text{Ho}]_{\text{init.}}$ of calcite or aragonite experiments at levels ten times higher than the present, respectively. What we observed, as a return, is the complete failure of calcite or aragonite precipitation. On the contrary, as shown in Figs. 2(a) and (b), no inhibitory effects were observed when $[Y]_{\text{init.}}$ and $[\text{Ho}]_{\text{init.}}$ were set at the present level (Table 2). The pre-

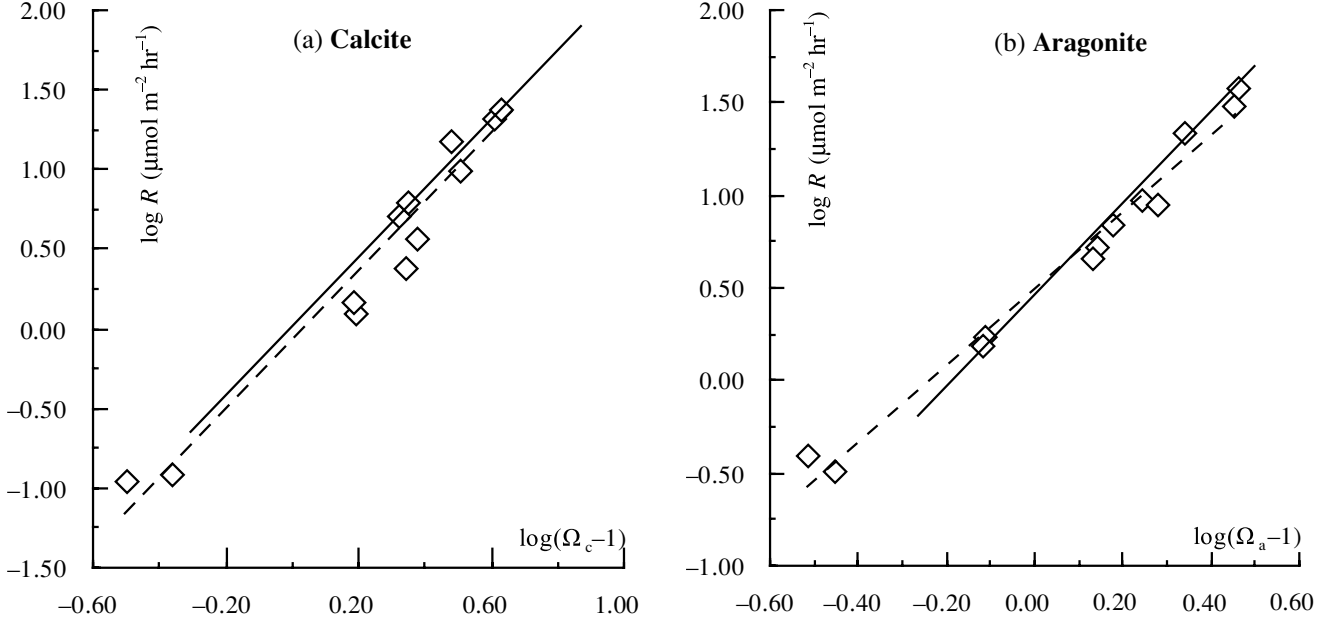


Fig. 2. Kinetic expressions of CaCO_3 precipitation in seawater: solid lines, without the presence of Y and Ho ; dash lines and open diamonds, with the presence of Y and Ho (Table 2).

precipitation of either calcite or aragonite, as usual, can be well expressed by the empirical formula of Morse (1983):

$$\log(R) = n \log(\Omega - 1) + \log(b). \quad (6)$$

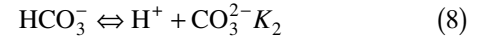
It suggests that the inhibition of dissolved YREEs on the precipitation of CaCO_3 is avoidable by setting initial YREE concentrations below certain critical values.

The complexation of Y and Ho

In CaCO_3 super-saturated solutions, dissolved YREEs(III) mainly occur as MCO_3^+ , $\text{M}(\text{CO}_3)_2^-$, and a small fraction of free hydrated M^{3+} (M for YREEs hereafter). Within our experimental conditions, MCO_3^+ and $\text{M}(\text{CO}_3)_2^-$ account for >99% of the total dissolved $M(\text{III})$ (Luo and Byrne, 2004). The molar ratios between $\text{M}(\text{CO}_3)_2^-$ and MCO_3^+ can be calculated following the equation:

$$\log \frac{[\text{M}(\text{CO}_3)_2^-]_{(\text{aq})}}{[\text{MCO}_3^+]_{(\text{aq})}} = \log_{\text{CO}_3}^{\text{H}} \beta_2^{(a)} - \log_{\text{CO}_3}^{\text{H}} \beta_1^{(b)} + \log[\text{HCO}_3^-] + \text{pH}, \quad (7)$$

where “ a ” and “ b ” are constants. With respect to the equilibrium:



and the equation:

$$[\text{CO}_3^{2-}] = K_2 * \frac{[\text{HCO}_3^-]}{[\text{H}^+]}, \quad (9)$$

Eq. (7) can be simplified as:

$$\log \frac{[\text{M}(\text{CO}_3)_2^-]_{(\text{aq})}}{[\text{MCO}_3^+]_{(\text{aq})}} = \log_{\text{CO}_3}^{\text{H}} \beta_2^{(a)} - \log_{\text{CO}_3}^{\text{H}} \beta_1^{(b)} + \log[\text{CO}_3^{2-}] - K_2. \quad (10)$$

Since the concentrations of Ca^{2+} are almost identical in our steady solutions, Eq. (10) can be further modified as:

$$\log \frac{[\text{M}(\text{CO}_3)_2^-]_{(\text{aq})}}{[\text{MCO}_3^+]_{(\text{aq})}} = \log_{\text{CO}_3}^{\text{H}} \beta_2^{(a)} - \log_{\text{CO}_3}^{\text{H}} \beta_1^{(b)} + \log(\Omega_c) + C, \quad (11)$$

where “ C ” can be treated as a constant.

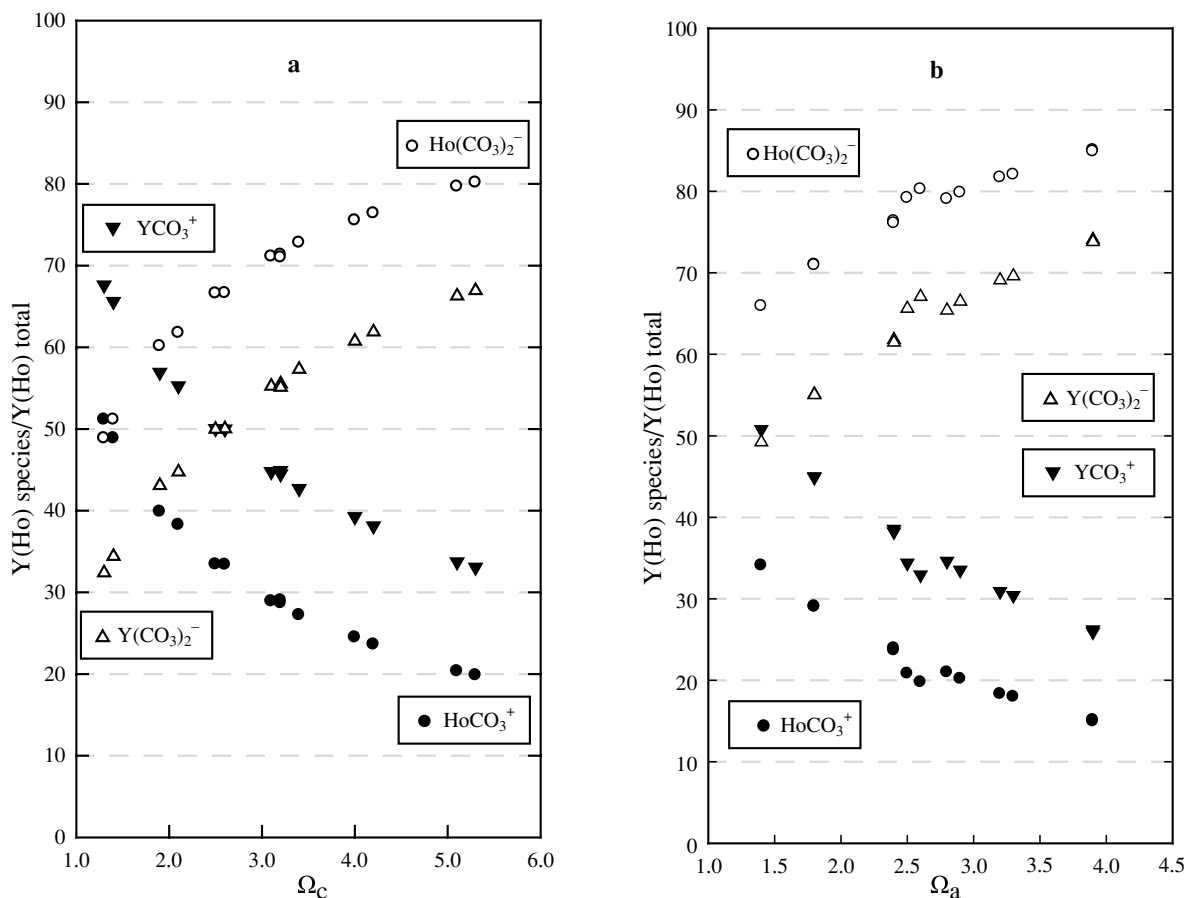


Fig. 3. The complexation of Y and Ho in our steady solutions as functions of Ω : (a) calcite experiments; (b) aragonite experiments.

The results of speciation calculation are shown Figs. 3(a) and (b). It is clear that the complexation of Y and Ho is very sensitive to solution chemistry. With the increase of Ω_c or Ω_a , the relative fractions of YCO_3^+ and $HoCO_3^+$ decrease while those of $Y(CO_3)_2^-$ and $Ho(CO_3)_2^-$ increase. In most cases, $Y(CO_3)_2^-$ and $Ho(CO_3)_2^-$ account for more than one half of total dissolved Y and Ho.

The partitioning of Y and Ho

Within our experimental conditions, both Y and Ho were observed to be strongly partitioned into either calcite or aragonite from seawater. In calcite, D_Y and D_{Ho} were determined to be ~ 520 – 1400 and ~ 700 – 1900 (Table 2). On the other hand, D_Y and D_{Ho} were determined to be ~ 1200 – 2400 and ~ 2400 – 4300 in aragonite (Table 2).

The results of our calcite experiments are broadly consistent with those of former experimental studies (Zhong and Mucci, 1995; Tanaka and Kawabe, 2006). For example, our D_Y and D_{Ho} values in calcite, ~ 520 – 1400 and ~ 700 – 1900 respectively, encompass the corresponding

values of Tanaka and Kawabe (2006), ~ 810 and ~ 1550 . Nevertheless, such values are much lower than those expected in seawater by Tanaka and Kawabe (2006). Their steady solutions, as compared to seawater, are much lower in $[Na]_{sol'n}$, carbonate alkalinity and pH while much higher in $[Ca]$. Therefore, the authors performed a series of corrections to their results: first multiplying their experimental D_{YREE} values by a factor of $[Na]_{seawater}/[Na]_{sol'n}$ (~ 9.3) and then corrections in YREE aqueous species. Finally, D_Y and D_{Ho} between calcite and seawater were corrected to be $10^{3.57-3.78}$ and $10^{3.78-4.02}$ (Tanaka and Kawabe, 2006) and vary with the preconditions of pH, pCO_2 . However, the coherency between this study and Tanaka and Kawabe (2006), as well as that of Eu(III) between Lakshatanov and Stipp (2004) and Zhong and Mucci (1995), indicates that the influences of Na^+ and Ca^{2+} on the partitioning of YREEs are far less important than those expected by Tanaka and Kawabe (2006).

Despite the difference among previous studies, they all indicate the strong YREE partitioning into calcite. However, our results are completely different from those

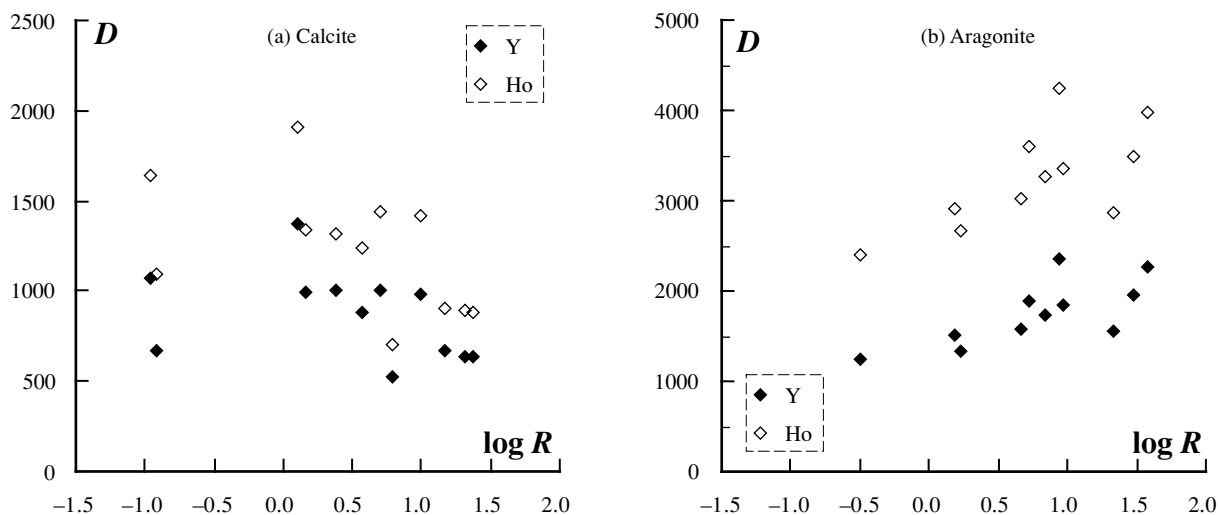


Fig. 4. Responses of D_Y and D_{Ho} to the precipitation rate ($\log R$, in $\mu\text{mol m}^{-2}\text{hr}^{-1}$): (a) calcite experiments; (b) aragonite experiments.

of Terakado and Masuda (1988) that calculated a D_{REE} of ~ 2.5 to ~ 10 . It is noteworthy that the experiments of Terakado and Masuda (1988) were conducted in a free-drift system, so the composition of their reacting solutions and reaction rates varied dramatically with time. We argue that, due to the fast and strong adsorption of REEs by calcite (Zhong and Mucci, 1995; Zavarin *et al.*, 2005), the free-drift system is not suitable to evaluate YREE coprecipitation with calcite. There is also a remarkable difference between results of this study and those of Terakado and Masuda (1988) for aragonite. D_{REE} in aragonite measured by Terakado and Masuda (1988) was ~ 2.5 – 5 and three orders of magnitude lower than our D_{Ho} values (~ 2400 – 4300). This can be also accounted to the different experimental conditions.

The comparability of our aragonite experiments with our calcite experiments is also very limited. Although large uncertainties affect our D_Y and D_{Ho} values, they most likely show different responses to R_c (calcite precipitation rates) and R_a (aragonite precipitation rates). As shown in Figs. 4(a) and (b), they appear to broadly decrease with the increase of R_c while increase with R_a . Zhong and Mucci (1995) interpreted that, among the aqueous complexes of MCO_3^+ and $\text{M}(\text{CO}_3)_2^-$, MCO_3^+ preferentially participate in the coprecipitation with calcite. Indeed, the incorporation of $\text{M}(\text{CO}_3)_2^-$ into calcite possibly require the reconstruction of at least one of its two $\text{M}-\text{CO}_3$ bonds, while MCO_3^+ can be directly incorporated into calcite without major modification. The assumption is in accord with the local structure of Y and Ho in calcite, i.e., both of them are sixfold coordinated in calcite lattices as Ca^{2+} (Tanaka *et al.*, 2008). With respect to the strong partition

behavior of Y and Ho in aragonite, we argue that both Y and Ho are probably ninefold coordinated in aragonite lattices as Ca^{2+} . Thereby, $\text{M}(\text{CO}_3)_2^-$ may preferentially participate in the coprecipitation with aragonite.

Influences of solution chemistry on the partitioning

The coprecipitation of trace elements with carbonates has been extensively investigated. It was observed that the partitioning is generally rate-dependent. Rimstidt *et al.* (1998) noticed that, for trace metals with thermodynamic distribution coefficients (D_0) larger than 1, their experimentally derived D values will decrease with the increase of precipitation rates.

As shown in Table 2, our D_Y and D_{Ho} values are far beyond the D_0 boundary of 1. However, they appear to react slowly to variations of R_c and R_a . Lakshtanov and Stipp (2004) observed that their partition coefficients of Eu(III) are restricted within a narrow range of 770 ± 290 and they are also insensitive to R_c . The applicability of the rate-dependent model to the partitioning of YREEs is getting even poorer when the results of Zhong and Mucci (1995) are taken into account. Our calcite experiment results are very close to those obtained by Zhong and Mucci (1995). Yet, due to the inhibitory effects of REEs, their calcite precipitation rates are systematically lower than ours. Following the rate-dependent model, their D_{Ho} values should be larger than ours. However, the fact is that our D_{Ho} values (~ 700 – 1900) are systematically larger than theirs (~ 40 – 570).

The difference between this study and Zhong and Mucci (1995) could indicate that the partitioning of Ho is dependent on solution chemistry. As compared to our

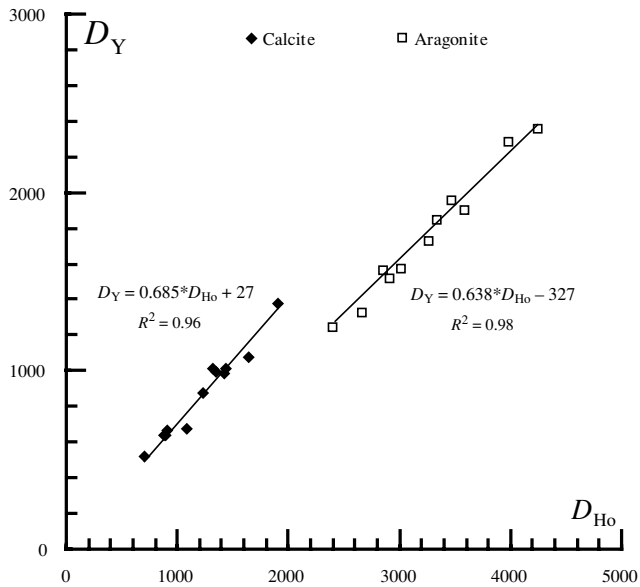


Fig. 5. Comparison between D_Y and D_{Ho} .

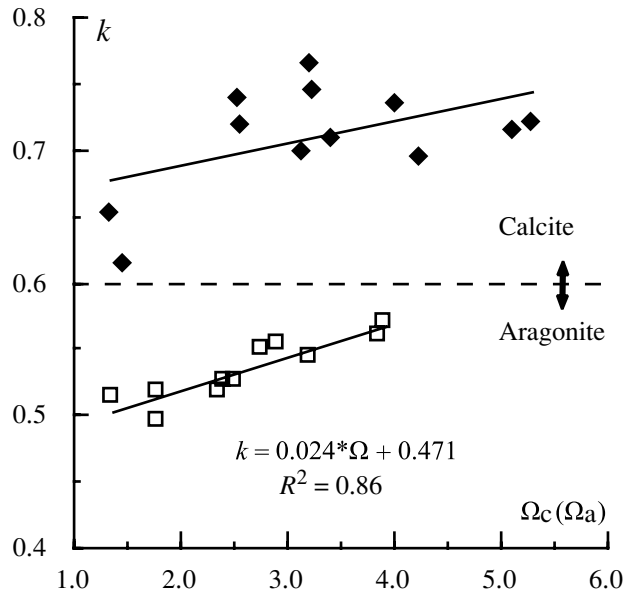


Fig. 6. Relation between k and Ω .

calcite experiments ($\Omega_c = 1.3\text{--}5.3$), most ($\sim 85\%$) experiments of Zhong and Mucci (1995) were conducted at higher saturation states ($\Omega_c = 5.2\text{--}16.6$). The variation of Ω_c can alter the surface charge of calcite (Van Cappellen *et al.*, 1993) and lead to a remarkable change in the complexation of Ho (Fig. 3(a)), i.e., the overwhelming percentage of $\text{Ho}(\text{CO}_3)_2^-$. As a result, the adsorption of Ho by the calcite surface was weakened. Similar results have been observed in the adsorption of Eu(III) and Sm(III) by calcite (Zavarin *et al.*, 2005). With respect to the role of adsorption in the coprecipitation, D_{Ho} and D_Y , as well as D values of other REEs, would decrease with the increase of Ω_c . When taking into account the preferential uptake of MCO_3^+ by calcite, the influences of solution chemistry on the partitioning of YREEs will be even more significant.

As comparison, the role of solution chemistry on the partitioning of Y and Ho in aragonite remains difficult to estimate. It is due to the fact that either the surface charge of aragonite or the adsorption of YREEs on the aragonite surface has never been reported. Nevertheless, the relative fractions of $\text{Y}(\text{CO}_3)_2^-$ and $\text{Ho}(\text{CO}_3)_2^-$ would increase with Ω_a (Fig. 3(b)). If $\text{Y}(\text{CO}_3)_2^-$ and $\text{Ho}(\text{CO}_3)_2^-$ preferentially participate in the coprecipitation with aragonite, the partitioning will benefit from the increase of $\text{Y}(\text{CO}_3)_2^-$ and $\text{Ho}(\text{CO}_3)_2^-$.

The fractionation between Y and Ho

Either in calcite or in aragonite, the partition behavior of Y and Ho is highly correlated (Fig. 5) and Y fractionates from Ho during the coprecipitation. The fractionation fac-

tor (Eq. (5)) was determined to be $\sim 0.62\text{--}0.77$ in calcite (k_c) and $\sim 0.50\text{--}0.57$ in aragonite (k_a). Within our experimental conditions, the fractionation appears to be stronger in aragonite than in calcite (Fig. 6). It is noteworthy that there is a strong correlation between k_a and Ω_a (Fig. 6).

In calcite, our k_c values ($\sim 0.62\text{--}0.77$) encompass the value of 0.71 reported by Tanaka *et al.* (2008). However, it is systematically larger than $\sim 0.49\text{--}0.62$ reported by Tanaka *et al.* (2004) and $\sim 0.49\text{--}0.59$ reported by Tanaka and Kawabe (2006). As compared to our experiments, those of Tanaka *et al.* (2004) and Tanaka and Kawabe (2006) were conducted at much lower pHs ($\sim 6.1\text{--}6.6$). Their initial or steady solutions are also much lower in carbonate alkalinity. Such differences result in another notable difference: the complexation of Y or Ho is overwhelmingly dominated by MCO_3^+ in their steady solutions while MCO_3^+ and $\text{M}(\text{CO}_3)_2^-$ dominate ours (Fig. 3(a)). On the other hand, $\text{M}(\text{CO}_3)_2^-$ accounts for $\sim 80\text{--}90\%$ of the total dissolved Y and Ho in reacting solutions of Tanaka *et al.* (2008). Thus, we argue that the Y–Ho fractionation during the coprecipitation with calcite may also be strongly influenced by solution chemistry. As shown in Fig. 7, the values of k_c appear to increase remarkably with $(\text{YCO}_3^+ \%)/(\text{HoCO}_3^+ \%)$.

The situation is even more obvious for the Y–Ho fractionation during the coprecipitation with aragonite, since there is a strong correlation between k_a and Ω_a (Fig. 6). However, k_a appears to increase remarkably with $(\text{Y}(\text{CO}_3)_2^- \%)/(\text{Ho}(\text{CO}_3)_2^- \%)$ instead of $(\text{YCO}_3^+ \%)/(\text{HoCO}_3^+ \%)$ (Fig. 8). This should be attributed to the preferential uptake of $\text{M}(\text{CO}_3)_2^-$ by aragonite.

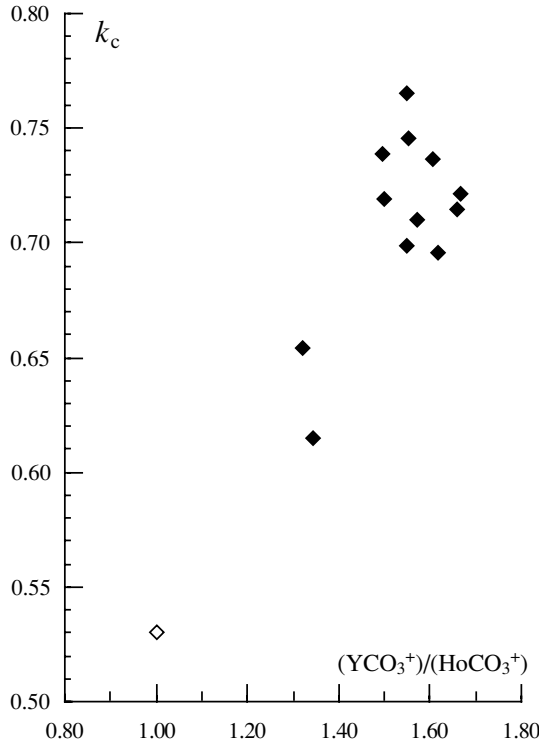


Fig. 7. The variation of k_c with $(YCO_3^+)/(HoCO_3^+)$. The k_c values determined by Tanaka and Kawabe (2006) are averaged (the open diamond), and the ratio of $(YCO_3^+)/(HoCO_3^+)$ is assumed to be 1 in their steady solutions.

The fractionation mechanism

No matter how the solution chemistry may affect the Y–Ho fractionation, the physico-chemical properties of Y and Ho are still the main factor affecting their fractionation in carbonates.

The fractionation of REEs in geochemical reactions is generally associated with their difference in ionic radii. Rimstidt *et al.* (1998) observed that there is a strong correlation between D_{REE} (in calcite; Zhong and Mucci, 1995) and effective ionic radii of REE^{3+} (Shannon, 1976). However, the ionic radii of Y^{3+} and Ho^{3+} , either sixfold or ninefold coordinated, are almost identical (Shannon, 1976). The EXAFS study of Tanaka *et al.* (2008) also confirmed that the difference between the first shell bond lengths of Y–O (2.310 Å) and Ho–O (2.311 Å) in calcite is negligible. The Y–Ho fractionation during the coprecipitation with $CaCO_3$ thereby cannot be explained by their difference in ionic sizes.

It is noteworthy that Ho(III) and Y(III) are substantially different in the electro configuration: that of Ho(III) is $[Xe](4f)^{10}$, but that of Y(III) is $[Kr]$ and does not have a 4f electron. As a result, Ho(III) and Y(III) are different in covalency. Tanaka *et al.* (2008) interpreted that, once the coordination environment of Ho(III) and Y(III)

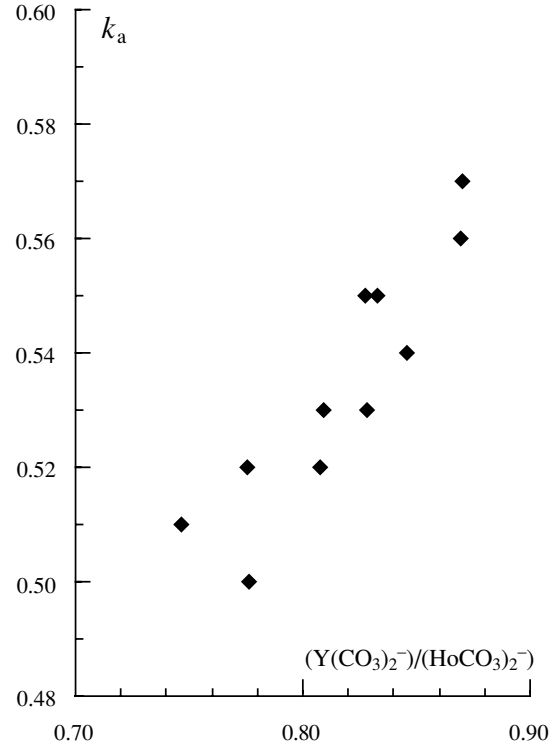
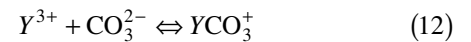


Fig. 8. The variation of k_a with $(Y(CO_3)_2^-)/(Ho(CO_3)_2^-)$.

changes, the fractionation will take place due to their difference in covalency. Moreover, they interpreted that the fractionation will get stronger as larger changes in coordination environments occur. Their interpretations are in accord with what was observed in aqueous solutions. For example,



and



dominate the aqueous complexation of Y and Ho at lower pHs (Luo and Byrne, 2004). The fractionation of the Y–Ho pair during this stage can be quantified as:

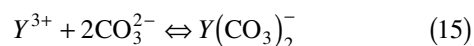
$$k_1 = \frac{\frac{[YCO_3^+]}{[Y^{3+}]}}{\frac{[HoCO_3^+]}{[Ho^{3+}]}} = 0.85. \quad (14)$$

Table 3. The comparison among experimentally and field derived partition coefficients of Y and Ho in calcite precipitates

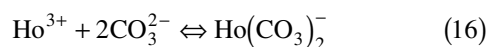
| Sample | Source of data | D_Y^* | D_{Ho}^* |
|--------------------------------------|-----------------------------|-----------|------------|
| limestones | Parekh <i>et al.</i> , 1977 | — | ~640 |
| limestones (Ishimaki) | Tanaka <i>et al.</i> , 2003 | ~970 | ~1800 |
| limestones (Tahara) | Tanaka <i>et al.</i> , 2003 | ~770 | ~1440 |
| microbialites | Webb and Kamber, 2000 | ~185 | ~260 |
| foraminifera (<i>Cibicoides</i>) | Haley <i>et al.</i> , 2005 | — | ~220 |
| foraminifera (<i>Uvigerinidae</i>) | Haley <i>et al.</i> , 2005 | — | ~215 |
| experimentally precipitated calcite | Zhong and Mucci, 1995 | — | ~40–570 |
| experimentally precipitated calcite | Tanaka and Kawabe, 2006 | ~810 | ~1550 |
| experimentally precipitated calcite | this study | ~520–1400 | ~700–1900 |

*The seawater Y and Ho concentrations used to calculate the partition coefficients (field researches) are different.

Furthermore, the fractionation is getting stronger during the following two reactions:



and



where the fractionation factor,

$$k' = \frac{\frac{[Y(CO_3)_2^-]}{[Y^{3+}]}}{\frac{[Ho(CO_3)_2^-]}{[Ho^{3+}]}} \quad (17)$$

is calculated to be 0.42 (Luo and Byrne, 2004).

It is undoubted that, when Y and Ho were partitioned into calcite or aragonite from seawater, they will also suffer a sequence of changes in coordination environments. The view of Tanaka *et al.* (2008) thereby can be further extended to the Y–Ho fractionation during various partitioning processes, e.g., the fractionation observed during the coprecipitation with $CaCO_3$. The difference in covalency between Y and Ho associated with changes in their coordination environments should be the determinant factor to the Y–Ho fractionation in the H_2CO_3 – $CaCO_3$ system.

Application to marine chemistry

Our results prove that Y does fractionate from Ho during the coprecipitation with $CaCO_3$. Before assessing the applicability of our k_c and k_a values to marine chemistry,

it is necessary to ensure whether the experimental partitioning is consistent with that between natural carbonates and seawater.

In aragonite, REE partition coefficients inferred from coral skeletons (e.g., Sholkovitz and Shen, 1995; Wyndham *et al.*, 2004) are broadly consistent and constrained within the range of ~1–10. As comparison, D_Y and D_{Ho} values derived from our aragonite experiments, ~1200–2400 and ~2400–4300 respectively, are substantially higher. The discrepancies may suggest that biomineralization of the coral skeletons control and modify the Y/Ho partitioning. The applicability of our results (aragonite) thereby is very limited.

On the contrary, the discrepancies among experimentally precipitated calcites (e.g., Tanaka and Kawabe, 2006; this study) and natural calcites (e.g., Webb and Kamber, 2000; Tanaka *et al.*, 2003) are little (Table 3). D_Y and D_{Ho} values derived from experimental studies and field researches (Table 2) fall within the range of 10^2 – 10^3 . This suggests that the incorporation of Y and Ho into natural calcite precipitates (microbialites, stromatolites, limestones, foraminifera, and etc.) is less affected by biomineralization processes. On the other hand, it implies that the abundance of Y and Ho is high enough to survive the diagenesis, so the original Y/Ho ratios are preserved. Sedimentary calcites are thus the best proxy of seawater Y/Ho ratios.

CONCLUSIONS

The coprecipitation of Y and Ho with calcite and aragonite was experimentally investigated in artificial seawater solutions at 25°C and 1 atm. The following conclusions were drawn:

1) Y and Ho are strongly partitioned into calcite and aragonite from seawater solutions. The partitioning is probably dependent on solution chemistry instead of precipitation rates.

2) Either in calcite or in aragonite, Y remarkably fractionates from Ho. The fractionation probably should be attributed the difference in covalency between Y and Ho.

3) Large discrepancies in the partitioning of Y and Ho were observed among experimental and field datasets of aragonite. It suggests that biomineralization of coral skeletons may strongly affect the incorporation of Y and Ho.

4) Our results of Y/Ho partitioning in calcite are broadly consistent with those of field researches. Sedimentary calcites are the best proxy for seawater Y/Ho ratios.

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